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PHASE EQUILIBRIA OF THE JOIN AKERMANITE-
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 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ AT ATMOSPHERIC PRESSURE.

The Ohio State University, Ph.D., 1970
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DISSERTATION

Presented in Partial Fulfillment of the
Requirements for the Degree Doctor of
Philosophy in the Graduate School

By

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LIST OF ABBREVIATIONS

A	Al ₂ O ₃
Ak(ak)	Akermanite
AlDi(al di)	Aluminous diopside
An(an)	Anorthite
C	CaO
CaTs	Calcium Tschermak's molecule
CMAS	CaO-MgO-Al ₂ O ₃ -SiO ₂
Di(di)	Diopside
En(en)	Enstatite
Fo(fo)	Forsterite
Fo ss(fo ss)	Forsterite solid solution
Geh(geh)	Gehlenite
Gl(gl)	Glass
L(l)	Liquid
M	MgO
Mel(mel)	Melilite
MgTs	Magnesium Tschermak's molecule
Mo(mo)	Monticellite
Mo ss(mo ss)	Monticellite solid solution
Pwo(pwo)	Pseudowollastonite
Pwo ss(pwo ss)	Pseudowollastonite solid solution
Py(py)	Pyroxene
S	SiO ₂
Sp(sp)	Spinel
ss	Solid solution
Wo(wo)	Wollastonite
Wo ss(wo ss)	Wollastonite solid solution

INTRODUCTION

Previous Work

During the past sixty years, a tremendous amount of data has been accumulated for the phase equilibrium of the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, due to its significant applications to petrology and technology. Only those data which are related to the present study will be mentioned below and will be further discussed in detail in the pertinent chapters or sections.

The phase equilibrium of the plane akermanite-anorthite-forsterite has not been studied as a discrete system before, but several joins in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, which intersect the plane akermanite-anorthite-forsterite, have been studied. Thus, the gross features of the equilibrium phase relations on the liquidus surface of the plane akermanite-anorthite-forsterite can be reconstructed by combining those previous experimental data. Figure 1 shows the relative positions of the plane ak-an-fo and the crystalline phases of the system CNAS pertinent to the present study.

Osborn and Tait (1952) have found that the primary field of spinel appears on the join an-fo. The liquidus

Figure 1. Positions of the join Ak-An-Fo, the polyhedron Sp-Ak-An-Fo-Di, and the pertinent crystalline phases in the system CMAS. For abbreviations in this and following figures, see LIST OF ABBREVIATIONS.

curve of spinel comes in contact with those of forsterite and anorthite at 1475°C and 1444°C at $\text{Fo}_{43}\text{An}_{57}$ and $\text{Fo}_{17}\text{An}_{83}$, according to Osborn and Tait (1952), or at 1480°C and 1433°C at $\text{Fo}_{45}\text{An}_{55}$ and $\text{Fo}_{14.5}\text{An}_{85.5}$, according to Schairer and Yoder (1965). De Wys and Foster (1957) reported that a binary eutectic point occurs at 1234°C and at $\text{Ak}_{54}\text{An}_{46}$ on the join anorthite-akermanite. The phase relations on the join ak-fo, as inferred from the data in the ternary system CaO-MgO-SiO_2 (Osborn and Muan, 1960), suggest that the primary field of monticellite appears on this join and extends into the plane ak-an-fo. Much information concerning the liquidus phase relation of the interior part of the plane ak-an-fo has been provided by Osborn, DeVries, Gee, and Kraner (1954) from their investigation of the planes parallel to the CaO-MgO-SiO_2 face of the tetrahedron CMAS at 5, 10, 15, 20, 25, 30, and 35% Al_2O_3 intervals. It was found that the primary field of diopside is very close to the plane ak-an-fo. The plane $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ traverses the plane ak-an-fo along the line joining the points $\text{Ak}_{49.5}\text{An}_{50.5}$ and $\text{Fo}_{33.6}\text{An}_{66.4}$ and, according to Segnit (1956) and O'Hara and Schairer (1963), spinel and anorthite should be the stable crystalline phases on the liquidus surface. So also does the 10% MgO plane parallel to the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ face of the tetrahedron CMAS, reported by Prince (1954), and spinel, anorthite, and

melilite are the crystalline phases at liquidus temperatures along the line of intersection, from $\text{Ak}_{68.5}\text{An}_{31.5}$ to $\text{Fo}_{17.3}\text{An}_{82.7}$. Also pertinent are the data of several joins which pierce the plane ak-an-fo. The join diopside-Ca Tschermak's molecule, studied by de Neufville and Schairer in 1962, pierces the plane ak-an-fo at the point $\text{Ak}_{35.8}\text{An}_{54.9}\text{Fo}_{9.3}$, which lies in the primary field of anorthite, with a liquidus temperature of 1310°C . The piercing point, $\text{Ak}_{19.6}\text{An}_{60.1}\text{Fo}_{20.3}$, of the join diopside- Al_2O_3 on the plane ak-an-fo falls, according to O'Hara and Schairer (1963), within the primary field of spinel with a liquidus temperature of about 1397°C . Likewise, both the joins spinel-diopside and enstatite-gehlenite pierce the plane ak-an-fo at the points $\text{Ak}_{28.1}\text{An}_{42.9}\text{Fo}_{29}$ and $\text{Ak}_{21.8}\text{An}_{44.5}\text{Fo}_{33.7}$ respectively. The appearance of forsterite at liquidus temperatures, 1420°C and 1435°C , at those intersections was reported by Schairer and Kushiro (1965) and Britton (1949). Chinner and Schairer (1962) have postulated that the primary field of diopside solid solution may have intruded the plane ak-an-fo. Figure 2 shows a summary of the pertinent experimental data mentioned above.

In addition to the foregoing investigations of the liquidus phase relations of intersecting planes and joins which have furnished indirect data for the plane ak-an-fo, several pertinent joins have been selected for the

Figure 2. The liquidus phase relations of the join ak-an-fo, as predicted by Chinner and Schairer (1962), are shown in broken curves. The previous experimental data pertinent to the present study are also shown. 1-7 Osborn, et. al. (1954); 8: Prince (1954); 9: Segnit (1956); 10: O'Hara and Schairer (1963); 11, De Neufville and Schairer (1962); 12: Schairer and Kushiro (1965); 13. Britton (1949).

study of their subliquidus phase equilibria. Chinner and Schairer (1962) studied the subliquidus phase equilibria of the join grossular-pyrope at atmospheric pressure and suggested the existence of two subtetrahedra sp-ak-an-fo and di-ak-an-fo in the polyhedron sp-ak-an-fo-di. These soon gained support from de Neufville and Schairer (1962) and Schairer and Kushiro (1965). In contrast, O'Hara and Schairer (1963) have suggested that spinel may be compatible with diopside, a relation which requires that the polyhedron mentioned above must be divided into three subtetrahedra sp-di-ak-an, sp-di-ak-fo, and sp-di-an-fo, instead of two, as mentioned previously. Recently O'Hara and Biggar (1969) and Yoder and Schairer (1969) have presented experimental evidence in favor of the second postulate.

The chemical composition of the crystalline phases is also noteworthy. Of the six crystalline phases pertaining to the present study, five are known to involve solid solution. It is well known that there is a complete solid solution series between akermanite and gehlenite. De Neufville and Schairer (1962), Chinner and Schairer (1962), and Yoder and Schairer (1969) have noted the variation of composition of melilite in equilibrium with different crystalline assemblages. It has been long recognized that diopside is able to accommodate trivalent cations, such as aluminum and ferric iron.

The limit of solid solution of aluminous diopside toward Ca Tschermak's molecule, Mg Tschermak's molecule, and Al_2O_3 in the plane $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ has been studied synthetically (Zvetkov, 1945; Segnit, 1953; Sakata, 1957; O'Hara and Schairer, 1963), but opinions vary greatly and are inconclusive. Attempts have been made to correlate the composition of such aluminous diopside with its physical properties (Zvetkov, 1945; Sakata, 1957; Hytonen and Schairer, 1961; Clark, Schairer, and de Neufville, 1962). In addition to the substantial entry of alumina into diopside, it has been found that diopside is also able to take forsterite into solid solution to an extent of at least 5% at temperatures of about 1300°C , as reported by Kushiro and Schairer (1963). That limited solid solution occurs at either end of the join forsterite-monticellite was shown by Ricker and Osborn (1954) and by Biggar and O'Hara (1969), who also discovered the instability of stoichiometric monticellite at atmospheric pressure. Schlauht and Roy (1965) reported that at 1720°C the maximum crystalline solution of spinel in forsterite is about 0.5 mole percent, whereas that of forsterite in spinel is slightly more than 5 mole percent. Further consideration of the composition of aluminous diopside and melilite will be presented in the Chapters IV and V.

The Purposes

The correct interpretation of the phase equilibrium of a four-component system is based on the correct subdivision of the tetrahedron, which, in turn, requires the correct compatibilities and compositions of the crystalline phases. Despite the great effort of many investigators, the phase equilibria of the polyhedron sp-ak-an-fo-di in the system CMAS are still far from clear; even the subdivision of this polyhedron--the very basic fact to be established in the phase equilibrium studies--remains disputable. It arises from the following uncertainties. Firstly, the conflicting views between the various authorities on the compatibility of spinel with diopside result in a state of confusion concerning the planes of compatibilities inside the polyhedron. Secondly, three of the five crystalline phases defining the polyhedron involve considerable amount of solid solution which causes the generation of three-phase regions at the expense of the portions of the subtetrahedra, but their equilibrium compositions in this polyhedron are not yet completely known.

Hence, the problem of the compatibility of spinel with aluminous diopside, and the equilibrium compositions of melilite, aluminous diopside, and forsterite solid solutions become major goals of the present study. The plane ak-an-fo has been chosen, because it cuts through

this polyhedron, and should provide a maximum of data to achieve these goals. It is therefore proposed to study the liquidus, subliquidus, and subsolidus phase equilibria, including the equilibrium compositions of the crystalline phases, of the plane ak-an-fo.

EXPERIMENTAL METHODS

General Statement

The experimental techniques vary according to the desired accuracy in the temperature measurement and the nature of the reactions. The liquidus and subliquidus runs, for which the phase changes are comparatively rapid and the temperature measurements are critical, were made in standard quenching furnace, and the charges were quenched in mercury. The subsolidus runs, for which the conversions of phases are much slower and the temperature measurements less critical, were made in "globar", Blue-M, and platinum-rhodium wound preparation furnaces, and the charges were quenched in air. Only the general experimental techniques will be outlined in this chapter, the special treatment for some runs will be discussed in the pertinent chapters or sections.

Preparation of Starting Material

To assure the homogeneity of starting material, glasses were prepared for all the compositions used in the determination of liquidus and subliquidus temperatures. Raw materials used to prepared glasses were C. P.

Baker's Analyzed Reagent magnesium carbonate (purity, 99.9%), calcium carbonate (purity, 99.8%), Linde Type B-5125 fine abrasive gamma-alumina (purity, 99.9%), and Pennsylvania Glass Sand Corporation five-micron MIN-U-SIL silica (purity, 99.9%). Raw materials were dried at about 150°C before they were weighed out to make up the mixtures of the desired compositions. Weighing was done to within ± 0.0002 grams of the calculated weight. The mixture was ground with acetone manually in an agate mortar and pestle for thirty minutes. Then it was transferred to a platinum crucible, fused, and quenched to glass two or three times with intervening crushing and grinding. The homogeneity of glass was assured by the uniformity in refractive index of glass. Refractive indices of glasses of all the compositions were measured and plotted in Figure 3.

When a particular phase assemblage was required in starting material for some subsolidus runs and cannot be obtained by devitrifying glasses at any temperatures, crystalline mixtures consisting of the required crystalline phases were prepared. The crystalline mixture was made by mixing, and grinding, in acetone, the appropriate proportions of the desired crystalline phases in an agate mortar and pestle manually for thirty minutes. The stoichiometric compositions of these mix-

Figure 3. Isofracts of the join $ak-an-fo$

tures in terms of akermanite, anorthite, and forsterite and the actual phases present are given in Table 1. Crystalline materials used to prepare these mixtures were synthetic akermanite, forsterite, anorthite, gehlenite, spinel, and diopside.

TABLE 1
COMPOSITIONS AND PHASE ASSEMBLAGES
OF CRYSTALLINE MIXTURES*

No.	Actual Phase Assemblages (in wt.%)						Composition (in wt.%)		
	Sp	Di	Ak	Geh	Fo	An	Ak	An	Fo
1	22.0	78.0	-	-	-	-	28.1	42.9	29.0
2	11.0	39.0	50.0	-	-	-	64.0	21.5	14.5
3	5.5	19.5	75.0	-	-	-	82.0	10.7	7.3
4	-	-	65.0	-	25.0	10.0	65.0	10.0	25.0
5	7.3	26.0	40.0	-	-	26.7	58.5	40.1	1.4
6	-	-	50.0	-	-	50.0	50.0	50.0	0
7	-	64.8	-	35.2	-	-	58.3	35.7	6.0
8	-	32.4	50.0	17.6	-	-	79.1	17.9	3.0
9	-	21.6	66.7	11.7	-	-	86.1	11.9	2.0
10	-	43.2	33.3	23.5	-	-	72.2	23.8	4.0

*For abbreviations for the crystalline phases in this and following tables, see LIST OF ABBREVIATIONS.

Devitrification

To avoid the erroneous determination of liquidus temperatures, resulting from metastable persistence of glass, glasses were devitrified, mostly at 900°C and a few at 1100°C, to provide seeds for the crystalline phases appropriate for the various mixtures.

Quenching Methods

The conventional quenching method developed at Geophysical Laboratory (Schafer, 1959) was used for all liquidus and subliquidus runs. Twenty milligrams of finely-powdered devitrified glass were wrapped in a platinum envelope of the size about 1×0.75 square centimeters. The batch was hung in the hot zone of a quenching furnace long enough for the attainment of equilibrium, then quenched in mercury to retain the phases formed at high temperatures. The temperature of the furnace was controlled to within $\pm 0.5^{\circ}\text{C}$ for a short period of time by Barber Coleman Null Balance Controller 357-A. The temperatures were read from a Pt-Pt90%Rh10% thermocouple on a Leeds & Northrup potentiometer. The thermocouple was periodically calibrated against the melting points of gold (1063°C), diopside (1391.5°C), akermanite (1454°C), and palladium (1549°C).

To make the subsolidus runs, the platinum envelopes containing the finely-powdered and pressed

samples were placed in "globar", Blue-M, or platinum-rhodium wound preparation furnaces about one to two inches from the thermocouple. The temperature was recorded on an automatic temperature recorder, Leeds & Northrup Speedomax Type H. The fluctuation was estimated to be about $\pm 15^{\circ}\text{C}$. At the end of the runs the charges were quenched in air.

Phase Identification

The petrographic microscope and x-ray diffraction were used to identify the phases. When the crystals were coarse enough to be identified microscopically, as in all liquidus and most subliquidus runs, an oil mount of powdered charge was prepared and examined. Whenever the crystalline phases in the charges are abundant enough to give a recognizable diffraction pattern, as in all subsolidus and some subliquidus runs, powder mounts of charges were x-rayed by Cu $K\alpha$ radiation on a Norelco high angle diffractometer scanning at a speed of one degree or one half degrees 2 θ per minute. Phase identification based on the diffraction patterns, however, is not as sensitive as optical examination, and phases present in less than 3% were difficult to detect by x-ray diffraction.

PHASE EQUILIBRIA OF THE JOIN AKERMANITE- ANORTHITE-FORSTERITE

General Statement

The multi-purpose nature of the present study demands a thorough investigation of phase relations of the join ak-an-fo from liquidus through subsolidus temperatures. The phase relations on the liquidus surface furnish the distribution of the fields of primary phases, the temperatures and positions of the piercing points of the quaternary univariant lines, and the possible compatibilities of the crystalline phases immediately below the temperatures of the quaternary invariant points. Although the quaternary nature of the join ak-an-fo complicates the phase relations, it is this quaternary nature that enables one to construct the quaternary phase equilibria, or the "flow sheet", of the polyhedron sp-ak-an-fo-di in the system CMAS from the subliquidus data. The subsolidus phase equilibria supply information regarding the subdivision of the polyhedron.

Liquidus Phase Relations

Using the standard quenching method, the liquidus temperatures of glasses were determined to within $\pm 2^{\circ}\text{C}$ or, in a few cases, $\pm 2.5^{\circ}\text{C}$. The duration of the runs ranges from one hour around 1400°C to two to three hours around 1250°C . Equilibrium is believed to have been attained, because large amounts of non-viscous liquid were present during the runs.

Overnight devitrification of glasses at 900°C did not provide glasses containing the seeds for the crystallization of monticellite, aluminous diopside, and spinel near the liquidus temperatures. To avoid retention of metastable phases and possible failure of stable phases to crystallize, glasses in the primary field of spinel were first held at a temperature well within the stability range of spinel to seed the charges with spinel. The temperature was then raised to redissolve spinel, and thus obtain the liquidus temperatures. Glasses of the compositions in the fields of monticellite and aluminous diopside apparently presented no such problems, because both crystalline phases were found to crystallize readily from the melts.

The crystals are generally large enough to be identified under the microscope. In Table 2 are listed the diagnostic features of the pertinent

TABLE 2

OPTICAL PROPERTIES OF CRYSTALLINE PHASES

	Anorthite	Spinel	Melilite (Ak ₁₀₀ - Ak ₇₀ Geh ₃₀)	Forsterite Solid Solution	Monticellite Solid Solution	Aluminous Diopside
Crystal Habit	lathlike	octahedral	blocky	prismatic, somewhat elongated	prismatic, usually six-sided	short prismatic, monoclinic
Extinction	inclined	isotropic	parallel	parallel	parallel	inclined
Refractive indices	$\alpha = 1.576$ $\gamma = 1.588$	1.719	$\xi = 1.639-1.648$ $\omega = 1.632-1.645$	$\alpha = 1.635-1.636$ $\gamma = 1.665-1.670$	$\alpha = 1.638-1.639$ $\gamma = 1.652-1.659$	$\alpha = 1.668-1.684$ $\gamma = 1.694-1.714$

crystalline phases. The experimental data of the liquidus runs are given in Table 3. The phase relations on the liquidus surface are determined from these data and are shown in Figure 4.

TABLE 3
LIQUIDUS DATA FOR THE JOIN AK-AN-FO

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
Primary Phase: Melilite					
54	46	0	1255.0	2.00	gl
			1251.0	3.00	mel, gl
			1248.5	3.50	mel, an, gl
49	44	7	1256.0	2.00	gl
			1252.0	2.00	mel, gl
			1247.0	20.00	mel, gl
50	38	12	1276.5	1.75	gl
			1271.5	2.00	mel, gl
55	40	5	1277.5	2.50	gl
			1273.5	2.50	mel, gl
			1270.0	2.00	mel, gl
56	31	13	1308.5	1.50	gl
			1305.5	1.50	mel, gl
			1301.0	1.50	mel, gl
62	33	5	1319.0	2.00	gl
			1315.0	2.00	mel, gl
			1311.0	2.00	mel, gl
60	25	15	1333.0	1.50	gl
			1329.0	1.75	mel, gl
			1325.0	1.75	mel, fo ss, gl
70	29	1	1340.0	1.50	gl
			1333.0	1.75	mel, gl
65	25	10	1355.5	1.50	gl
			1351.5	1.25	mel, gl
			1346.5	1.25	mel, gl
65	20	15	1365.5	1.50	gl
			1360.5	1.50	mel, gl
			1355.5	1.25	mel, gl
73	20	7	1375.0	1.50	gl
			1371.5	1.50	mel, gl
			1363.5	1.67	mel, gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
71	15	14	1382.0	1.50	gl
			1379.0	1.50	mel, gl
81	14	5	1401.0	1.50	gl
			1397.0	1.00	mel, gl
83	0	17	1391.0	1.75	mel, gl
			1440.0	1.50	gl
			1436.0	2.00	mel, gl
			1432.5	1.50	mel, gl
72	25	3	1359.0	1.50	gl
			1355.0	4.00	mel, gl
			1347.0	6.00	mel, gl
70	20	10	1370.0	2.00	gl
			1366.0	2.00	mel, gl
			1364.0	2.00	mel, gl
76	6	18	1420.0	1.00	gl
			1416.0	1.00	mel, gl
			1413.0	1.00	mel, gl
77	5	18	1426.0	1.25	gl
			1422.0	1.00	mel, gl
			1418.0	2.50	mel, fo ss, gl

Primary Phase: Forsterite solid solution

47	42	11	1266.0	2.00	gl
			1262.0	2.50	fo ss, gl
38	48	14	1271.0	2.00	gl
			1267.0	2.00	fo ss, gl
			*1267.0	3.00	fo ss, gl
			1263.0	2.00	fo ss, gl
			1260.0	18.00	fo ss, gl
			*1260.0	20.00	fo ss, gl
44	44	12	1273.5	2.00	gl
			1269.5	2.00	fo ss, gl
			1262.0	2.00	fo ss, gl
			1257.0	2.00	fo ss, gl
40.5	45.5	14	1277.0	2.00	gl
			1273.0	2.00	fo ss, gl
			1269.0	2.00	fo ss, gl
			1257.0	2.00	fo ss, gl
36	49	15	1277.5	3.00	gl
			1274.5	2.00	fo ss, gl
			1269.5	1.75	fo ss, gl
34	49	17	1265.0	2.50	fo ss, an, gl
			1290.5	2.25	gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
52	35	13	1287.0	2.00	fo ss, gl
			1283.0	2.00	fo ss, sp, gl
			1296.0	10.00	gl
			1292.0	3.00	fo ss, gl
43	40	17	1287.0	2.00	fo ss, mel, gl
			1315.5	1.75	gl
			1312.5	2.00	fo ss, gl
			1308.5	1.75	fo ss, gl
52	30	18	1346.0	1.75	gl
			1342.0	1.50	fo ss, gl
			1339.0	1.50	fo ss, gl
			1354.0	1.75	gl
28	48	24	1350.0	1.75	fo ss, gl
			1342.0	1.50	fo ss, gl
			1332.5	1.50	fo ss, gl
			1359.5	1.50	gl
39	39	22	1355.5	1.50	fo ss, gl
			1347.5	1.50	fo ss, gl
			1367.5	1.75	gl
			1364.5	1.75	fo ss, gl
57	25	18	1359.5	1.50	fo ss, gl
			1349.5	2.00	fo ss, gl
			1373.5	1.00	gl
			1369.5	1.25	fo ss, gl
32	43	25	1366.0	1.50	fo ss, gl
			1373.5	1.25	gl
			1369.5	3.00	fo ss, gl
			1365.5	1.50	fo ss, gl
62	20	18	1379.0	1.50	gl
			1375.5	1.50	fo ss, gl
			1367.0	1.50	fo ss, gl
			1388.0	1.25	gl
23	49	28	1384.0	1.25	fo ss, gl
			1376.0	1.50	fo ss, sp, gl
			1375.0	1.50	fo ss, sp, gl
			1368.0	1.50	fo ss, sp, gl
65	15	20	1408.0	1.50	gl
			1404.0	1.50	fo ss, gl
			1399.0	1.50	fo ss, gl
			1395.0	2.00	fo ss, gl
70	10	20	1389.5	1.75	fo ss, gl
			1382.5	1.75	fo ss, mel, gl
			1420.5	2.25	gl
			1416.0	1.00	fo ss, gl
			1413.5	1.50	fo ss, gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
75	5	20	1430.0	1.25	gl
			1426.0	1.25	fo ss, gl
			1422.5	1.50	fo ss, gl
45	30	25	1421.0	1.25	gl
			1417.0	1.25	fo ss, gl
38	35	27	1428.0	1.50	gl
			1424.0	2.25	fo ss, gl
30	40	30	1431.0	1.50	gl
			1428.0	2.00	fo ss, gl
			1424.0	1.50	fo ss, gl
25	45	35	1420.0	1.25	gl
			1416.0	1.25	fo ss, gl
			1412.0	1.25	fo ss, gl
			1403.0	1.25	fo ss, gl
			1394.0	1.25	fo ss, gl
			1449.0	1.50	gl
55	20	25	1445.5	1.25	fo ss, gl
			1442.0	1.25	fo ss, gl
			1433.0	1.25	fo ss, gl
			1455.0	3.00	gl
48	24	28	1450.0	1.25	fo ss, gl
			1454.5	1.25	gl
37	32	31	1450.5	1.25	fo ss, gl
			1445.0	1.00	gl
20	45	35	1441.0	1.00	fo ss, gl
			1433.0	1.25	fo ss, gl
			1458.0	1.00	gl
25	40	35	1454.0	1.00	fo ss, gl
			1463.0	1.00	gl
			1459.0	1.00	fo ss, gl
10	50	40	1455.0	1.00	fo ss, gl
			1415.0	1.50	gl
			1411.0	1.25	fo ss, gl
			1407.0	1.25	fo ss, mel, gl
73	8	19			

Primary Phase: Anorthite

51	46	3	1252.0	3.33	gl
			1248.5	2.33	an, mel, gl
42.5	47.5	10	1253.5	2.50	gl
			1250.5	2.50	an, gl
			1247.0	17.00	an, al di, gl
40	47.5	12.5	1255.0	2.00	gl
			1252.0	2.00	an, al di, gl
			1250.0	2.00	an, al di, gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
48	47	5	1256.0	2.00	gl
			1252.0	2.00	an, gl
			1249.0	2.00	an, gl
41	47.5	11.5	1259.0	3.50	gl
			1255.0	2.50	an, gl
41	48	11	1265.5	2.00	gl
			1262.0	2.00	an, gl
			1257.5	3.00	an, gl
			1252.5	2.50	an, gl
			1247.0	2.50	an, al di, gl
35	51	14	1277.0	2.00	gl
			1274.0	2.00	an, gl
			1269.0	2.00	an, gl
			1267.0	20.00	an, fo ss, gl
			1263.0	2.00	an, fo ss, gl
35	53	12	1296.0	1.50	gl
			1291.0	2.00	an, gl
			1286.0	2.00	an, gl
			1279.0	1.50	an, gl
			1262.0	18.00	an, gl
32	54	14	1301.0	2.00	gl
			1297.0	6.00	an, gl
			1281.0	16.00	an, gl
35	55	10	1306.0	2.00	gl
			1302.0	2.00	an, gl
			1299.0	1.50	an, gl
			1290.5	2.00	an, gl
29	59	12	1336.5	1.75	gl
			1333.5	1.75	an, gl
			1331.5	2.50	an, gl
32	61	7	1357.0	1.50	gl
			1353.0	1.50	an, gl
			1349.0	1.75	an, gl
37	62	1	1367.5	1.50	gl
			1363.5	1.50	an, gl
			1351.5	1.50	an, gl
25	70	5	1413.0	1.00	gl
			1409.0	1.00	an, gl
			1406.0	1.00	an, gl
18	70	12	1401.0	1.00	gl
			1397.0	1.00	an, gl
			1391.0	1.50	an, gl
19	76	5	1439.0	1.00	gl
			1434.0	2.00	an, gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
10	80	10	1445.0	1.00	gl
			1441.0	1.00	an, gl
			1432.0	1.00	an, gl
Primary Phase: Aluminous Diopside					
47	46	7	1249.0	2.00	gl
			1246.0	2.00	al di, an, gl
48	45	7	1252.0	2.50	gl
			1248.0	3.00	al di, gl
			1245.0	3.00	al di, gl
45	47	8	1252.0	2.75	gl
			1248.0	2.25	al di, an, gl
			1246.0	5.00	al di, an, gl
47	44	9	1257.0	2.00	gl
			1253.0	2.00	al di, gl
			1249.0	2.00	al di, gl
45	45	10	1253.0	3.00	gl
			1254.0	2.00	al di, gl
			1250.0	2.00	al di, gl
			1244.5	17.50	al di, gl
43	46	11	1256.0	2.50	gl
			1252.5	20.00	al di, gl
42	46	12	1256.5	2.00	gl
			1253.0	2.00	al di, gl
Primary Phase: Spinel					
34	51	15	1286.0	20.00	gl
			1282.0	14.00	sp, gl
32.5	52.5	15	1287.0	14.00	gl
			1283.0	14.00	sp, an, gl
			1274.5	11.00	sp, an, gl
30	52	18	1300.0	2.00	gl
			1296.0	24.00	sp, gl
			1283.0	24.00	sp, fo ss, gl
30	54	16	1306.0	24.00	gl
			1304.0	20.00	sp, gl
			1294.0	14.00	sp, gl
			1289.0	24.00	sp, an, gl
20	65	15	1367.0	1.50	gl
			1364.0	1.50	sp, an, gl
			1361.0	1.50	sp, an, gl
			1355.0	1.50	sp, an, gl
			1347.0	2.50	sp, an, gl

TABLE 3 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
15	65	20	1399.5	2.00	gl
			1397.5	4.00	sp, gl
15	55	30	1402.0	1.00	gl
			1398.0	1.00	sp, gl
10	65	25	1425.0	1.50	gl
			1421.5	1.00	sp, gl
			1416.5	1.00	sp, gl
10	53	37	1430.0	1.00	gl
			1426.5	1.00	sp, gl
			1416.5	1.50	sp, gl
Primary Phase: Monticellite solid solution					
79	3	18	1429.0	4.00	gl
			1426.0	1.50	mo ss, gl
			1424.0	2.00	mo ss, mel, gl
			1422.0	1.25	mo ss, mel, gl
			1420.0	1.25	fo ss, mel, gl
80	0	20	1449.0	1.50	gl
			1446.0	2.00	mo ss, fo ss, gl
			1442.0	5.00	mo ss, fo ss, gl
			1440.0	1.50	mo ss, fo ss, gl
			1437.0	3.00	mo ss, fo ss, gl
			1432.0	1.50	mo ss, fo ss, gl
			1428.0	1.50	fo ss, mel, gl
77	4	19	1426.0	1.50	gl
			1422.0	1.00	mo ss, fo ss, gl
			1416.0	1.50	fo ss, mel, gl
79	2	19	1436.0	1.25	gl
			1434.0	1.25	mo ss, fo ss, gl
			1432.0	2.00	mo ss, fo ss, gl
			1428.0	1.25	fo ss, mel, gl

*Starting material for these runs contained spinel, aluminous diopside, anorthite, and glass.

As can be seen in Figure 4, six primary fields of crystallization are uncovered on the liquidus surface. All the crystalline phases except anorthite involve solid solutions. Only the primary field of anorthite, and then only for the assemblage anorthite+liquid, is ternary. The remaining part of the join ak-an-fo is quaternary,

Figure 4. Liquidus phase relations of the join ak-an-fo

for the compositions of other crystalline phases do not lie on the plane. The fact that the primary fields of spinel and aluminous diopside are not in contact with each other does not suggest, nor does it rule out, the compatibility of spinel with aluminous diopside. The positions and temperatures of the piercing points of the quaternary univariant lines on the join ak-an-fo are given in Table 4.

TABLE 4
TEMPERATURES AND POSITIONS
OF THE PIERCING POINTS

Univariant Lines	Temp. (°C)	Composition (wt.%)		
		Ak	An	Fo
fo ss+an+sp+l	1267	35.0	50.5	14.5
fo ss+an+al di+l	1255	39.5	47.5	13.0
fo ss+mcl+al di+l	1249	47.0	43.0	10.0
mcl+an+al di+l	1245	48.5	45.5	6.0
fo ss+mo ss+mcl+l	1422	77.0	4.5	18.5

Subliquidus Phase Relations

The subliquidus phase equilibria of the join ak-an-fo were also studied. Glasses were held at successively lower temperatures from the liquidus through the divariant surface and univariant lines to the quaternary invariant points. The appearance and disappearance of the phases were recorded to form the courses of crystallization of some selected glasses. Then the subliquidus

phase equilibria, or the "flow sheet", were constructed by combining the courses of crystallization of those glasses.

Due to the sluggishness of the reactions when the temperatures approach the invariant points, the subliquidus runs generally require a longer duration than do the liquidus runs. Sometimes, attainment of equilibrium is still in doubt even after runs of a week. The reluctant nucleation of spinel and the persistence of the metastable phases add to the complexity of the experiments. To overcome these difficulties, the charges were intermittently quenched and ground to provide fresh contact, so that the reactions could be accelerated.

Optical examination, although still very sensitive and successful in the phase identification, nevertheless, becomes more difficult as the number of phases and crystals increase, and it is often greatly assisted by x-ray diffraction.

The intermittent quenching and phase analysis of the charges during the subliquidus runs can also show the changing phase assemblages of the charges, which, in turn, indicate the nature of the univariant lines and the invariant points--reaction or subtraction. To test the nature of the univariant line $sp+fo \rightleftharpoons ss+an+l$, the charge of the appropriate composition was first held well within the stability range of spinel for a few hours to

form well-crystallized spinel. Then the temperature was lowered to that of the univariant line $sp+fo \rightleftharpoons ss+an+l$ and held there for at least fifteen hours. That this univariant line is in a reaction relation with respect to spinel is evident from the fact that spinel either disappeared completely or was corroded. A similar technique was also used successfully to check the reaction nature of the invariant point $an+fo \rightleftharpoons ss+sp+al \rightleftharpoons di+l$ with respect to anorthite and forsterite.

Listed in Table 5 are only those runs which are believed to represent the equilibrium assemblages. Based partially on these data, subliquidus phase equilibria of the join $ak-an-fo$ are constructed and are given in Figures 5 through 12 in the form of a series of approximate isothermal sections. Further discussion of the significance of the subliquidus phase equilibria in relation to the polyhedron $sp-ak-an-fo-di$ will be given in the last section of this chapter.

TABLE 5

SUBLIQUIDUS DATA FOR
THE JOIN AK-AN-FO

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
Primary Phase: Melilite					
54	46	0	1244.0	20.0	mel, an, gl
			1239.0	144.0	mel, an, al di, gl
49	44	7	1242.0	18.0	mel, al di, gl

TABLE 5 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
50	38	12	1261.5	18.0	mel, fo ss, gl
			1252.0	20.0	mel, fo ss, gl
			1247.0	23.0	mel, fo ss, al di, gl
			1240.0	19.0	mel, fo ss, al di, gl
55	40	5	1243.5	18.0	mel, al di, gl
56	31	13	1240.5	49.0	mel, fo ss, al di, gl
62	33	5	1245.0	24.0	mel, gl
70	29	1	1260.0	24.0	mel, gl
			1252.0	24.0	mel, gl
			1245.0	25.0	mel, an, gl
71	15	14	1240.0	168.0	mel, fo ss, al di, gl
*58.5	40.1	1.4	1215.0	936.0	mel, an, pwo ss, gl

Primary Phase: Forsterite Solid Solution

47	42	11	1250.5	19.0	fo ss, mel, gl
			1246.0	23.0	fo ss, mel, al di, gl
38	48	14	1256.0	2.0	fo ss, an, al di, gl
			1253.0	2.0	fo ss, an, al di, gl
			1247.0	72.0	fo ss, an, al di, gl
			1244.0	84.0	fo ss, an, al di, sp, gl
			1240.0	120.0	an, sp, al di, gl
			1239.0	186.0	an, sp, al di, gl
44	44	12	1253.0	24.0	fo ss, gl
			1245.5	17.0	fo ss, al di, gl
40.5	45.5	14	1253.0	17.0	fo ss, al di, gl
			1249.0	19.0	fo ss, al di, gl
34	49	17	1252.0	19.0	fo ss, an, gl
			1247.0	18.0	fo ss, an, al di, gl
43	40	17	1252.5	23.0	fo ss, gl
			1248.0	48.0	fo ss, al di, gl
			1240.5	49.0	fo ss, al di, mel, gl
32	43	25	1274.5	15.5	fo ss, gl
			1266.5	18.0	fo ss, gl
			1257.0	16.0	fo ss, an, gl
19	51	30	1294.5	24.0	fo ss, sp, an, gl
			1285.5	50.0	fo ss, sp, an, gl
52	35	13	1241.0	336.0	fo ss, mel, al di, gl
39	39	22	1241.0	336.0	fo ss, sp, al di, gl
			1245.0	120.0	fo ss, al di, gl

Primary Phase: Aluminous Diopside

47	46	7	1243.0	17.0	al di, an, gl
48	45	7	1238.0	28.0	al di, mel, gl
47	44	9	1242.0	21.0	al di, mel, gl

TABLE 5 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
43	46	11	1248.5	22.0	al di, gl
			1245.5	22.0	al di, gl
42	46	12	1239.5	120.0	al di, an, sp, gl

Primary Phase: Spinel

34	51	15	1272.5	20.0	sp, fo ss, gl
			1266.0	20.0	fo ss, an, gl
32.5	52.5	15	1266.0	15.0	fo ss, an, gl
30	52	18	1277.5	24.0	sp, fo, an, gl
			1272.0	2.0	fo ss, an, gl
			1268.0	33.0	sp, fo, an, gl
30	54	16	1270.0	24.0	sp, fo ss, an, gl
			1269.0	26.0	sp, fo ss, an, gl
			1268.0	36.0	sp, fo ss, an, gl
			1267.5	19.0	fo ss, an, gl
			1264.0	17.0	fo ss, an, gl
20	65	15	1337.0	4.0	sp, an, gl
			1307.5	16.0	sp, an, gl
			1299.0	27.0	sp, an, gl
			1291.0	48.0	sp, an, fo ss, gl
15	55	30	1313.5	19.0	sp, fo ss, gl
			1303.0	23.0	sp, fo ss, an, gl
			1294.0	42.0	fo ss, an, gl
			1290.0	46.0	sp, fo ss, an, gl
			1277.0	67.0	sp, fo ss, an, gl
			1265.0	90.0	fo ss, an, gl
			1262.0	72.0	fo ss, an, gl
			1255.5	76.0	fo ss, an, gl
10	65	25	1350.0	16.0	sp, gl
			1335.0	16.0	sp, an, gl
			1316.0	17.0	sp, an, gl
			1307.0	50.0	sp, an, fo ss, gl
			1290.0	39.0	fo ss, an, gl
			1290.0	46.0	sp, fo ss, an, gl
			1272.0	67.0	sp, fo ss, an, gl
			1265.0	90.0	fo ss, an, gl
			1262.0	72.0	fo ss, an, gl
			1255.5	76.0	fo ss, an, gl

Primary Phase: Anorthite

48	47	5	1245.0	23.0	an, mel, gl
40	47.5	12.5	1247.0	20.0	an, al di, gl
			1242.0	42.0	an, al di, gl
41	47.5	11.5	1251.0	17.0	an, al di, gl

TABLE 5 -Continued

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
35	51	14	1255.0	2.0	an, fo ss, gl
			1250.0	14.0	an, fo ss, al di, gl
32	54	14	1276.5	36.0	an, gl
			1274.5	20.0	an, gl
			1267.0	20.0	an, fo ss, gl
35	55	10	1268.5	5.0	an, gl
29	59	12	1323.5	12.0	an, gl
			1290.0	7.0	an, gl
			1270.5	18.0	an, sp, gl
37	62	1	1260.5	24.0	an, gl
			1252.0	24.0	an, gl
			1248.0	48.0	an, mel, gl
*50	50	0	1215.0	936.0	an, mel, pwo ss, gl

*Starting material for these two runs was crystalline mixtures. The runs were made in a "globar" furnace and were quenched in air.

Subsolidus Phase Equilibria

The problem of subsolidus phase equilibria is essentially the determination of the relative stability of different phase assemblages or the compatibilities of the crystalline phases. An assemblage is considered to be more stable than the other assemblages when it is found to develop from others. Similarly a crystalline phase is considered to be more stable than the other crystalline phases if it is found to develop at the expense of others. Based on this principle the subsolidus phase equilibria of the join ak-an-fo have been studied. The phase assemblage of the starting material, either devitrified glasses or mixtures of appropriate crystalline phases, was always analyzed before it was

Figure 5. Approximate isothermal section of the join ak-an-fo at 1425°C. For simplicity, from figures 5 through 11, the boundaries between fields of different phase assemblages involving melilite or/ and forsterite solid solution are drawn to radiate from akermanite and forsterite respectively. ° Runs between 1425°C and 1435°C

Figure 6. Approximate isothermal section of the join ak-an-fo at 1350°C. o Runs between 1350°C and 1390°C

Figure 7. Approximate isothermal section of the join ak-an-fo at 1275°C • Runs between 1275°C and 1310°C

Figure 8. Approximate isothermal section of the join ak-an-fo at 1260°C. • Runs between 1260°C and 1274°C

Figure 9. Approximate isothermal section of the join ak-an-fo at 1250°C. o Runs between 1250°C and 1259°C

Figure 10. Approximate isothermal section of the join ak-an-fo at 1245°C. • Runs between 1245°C and 1249°C

Figure 11. Approximate isothermal section of the join ak-an-fo at 1241°C. • Runs between 1241°C and 1244°C

fired at the desired temperatures. The charges were checked intermittently to determine the changing phase assemblage until the more stable phases have fully developed and the unstable phases had been completely eliminated. The charges were also ground and pressed intermittently during the long period of the run to accelerate the reactions. The crystals in the subsolidus runs are so small that optical examination presented great difficulties, and accurate phase identification relied completely on x-ray diffraction. The subsolidus experimental data are presented in Table 6 and in Figures 13 and 14. The significance of these data will be discussed in detail in the subsequent section.

Discussion

Compatibility of spinel with aluminous diopside

Historical review One of the controversial topics of the phase equilibria in the system CMAS in the past decade was the compatibility of spinel with aluminous diopside. As can be seen from Figure 1, the join spinel-aluminous diopside intersects the plane ak-an-fo. In other words, a particular proportion of spinel and aluminous diopside is isochemical with the assemblage akermanite+anorthite+forsterite. This is also clear from the following equation:

TABLE 6

SUBSOLIDUS DATA FOR THE JOIN AK-AN-FO
(tr.)=Trace (?)=Identification uncertain

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
Temperature: 1100±20°C						
15	55	33	Glasses devitrified at 1225°C for a month	al di, sp, an, fo ss, mel	69	al di, sp, an, fo ss
10	65	25		al di, sp, an, fo ss	69	al di, sp, an, fo ss
20	65	15		al di, an, mel, fo ss, sp (tr.)	106	al di, sp, an, fo ss
25	70	5		al di, an, mel, sp (tr.)	69	al di, sp, an, fo ss
32	61	7		al di, an, mel, fo ss, sp (tr.)	69	mel, an, al di, sp.
39	39	22		al di, fo ss, mel an, sp (tr.)	106	al di, fo ss, mel, sp
28	48	24	Glasses Devitrified at	al di, an, mel, fo ss, sp (tr.)	79	al di, sp, an, fo ss
32	43	25	1100°C for 27 days	al di, fo ss, an, mel, sp (tr.)	79	al di, sp, an, fo ss, mel
38	48	14	Quenching run at 1244.5°C	al di, sp, an, gl	69	al di, an, sp, mel

TABLE 6 -Continued

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
42	46	12	Glass devitrified at 900°C	al di, an, mel, fo ss	106	al di, sp an, mel
57	25	18	Glasses Devitrified at 1100°C for 27 days	al di, fo ss, mel, an (tr.)	79	al di, fo ss, mel, sp (tr.)
52	35	13		al di, fo ss, an, mel	79	al di, mel, an (tr.), sp (tr.)
65	15	20		al di, an, mel, fo ss	79	al di, fo ss, mel
Temperature: 1160±15°C						
15	55	30	Glasses Devitrified at 1180°C for 31 days	al di, sp, an, mel, fo ss	25	al di, sp, an, fo ss
10	65	25		al di, an, mel, fo ss, sp (tr.)	25	al di, sp, an, fo ss
20	65	15		al di, fo ss, an, mel, sp (tr.)	25	al di, sp, an
25	70	5		al di, an, mel, fo ss	25	al di, sp, an, mel
35	55	15		al di, an, mel fo ss,	25	al di, sp, an, mel
32	61	7		al di, an, mel fo ss	25	al di, sp, an, mel

TABLE 6 -Continued

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
34	49	17	Glasses Devitrified at 1180° for 31 days	al di, an, mel, fo ss	25	al di, sp, an, mel
28	48	24		al di, an, mel, fo ss, sp (tr.)	25	al di, sp, an, mel
48	47	5		al di, an, mel, fo ss	25	al di, sp, an, mel
40	47.5	12.5		al di, an, mel, fo ss	25	al di, sp, an, mel
44	44	12		al di, an, mel, fo ss	25	al di, sp, an, mel
Temperature: 1200±15°C						
10	53	37	Glasses Devitrified at 1200°C for 24 days	al di, fo ss, an	24	al di, an, fo ss sp (tr.)
15	55	30		al di, fo ss, an, sp, mel	24	al di, sp, an, fo ss
15	65	20		al di, fo ss, an, sp, mel	24	al di, sp, an, fo ss
19	51	30		al di, fo ss, an, sp, mel	24	al di, sp, an, fo ss
32	61	7		al di, fo ss, an, mel, sp (tr.)	24	al di, sp, an, mel

TABLE 6 -Continued

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
80	0	20	Glasses devitrified at 1200°C for 24 days	mel, fo ss	24	mel, fo ss, di
42	46	12		al di, an, mel, fo ss, sp (tr.)	24	al di, sp, an, mel
52	35	13		al di, sp, mel, fo ss	24	al di, sp, mel, fo ss (?)
45	47	8		al di, an, mel, fo ss, sp (tr.)	24	al di, an, mel, sp (tr.)
33	48	14	Quenching run at 1240°C	al di, sp, an, mel, fo ss (tr.), gl	48	al di, sp, an, mel
15	55	30	Gl. devitrified at 1180°C for a month	al di, sp, mel, an, fo ss	48	al di, sp, an, fo ss
23	49	28	Gl. devitrified at 900°C for 24 days	an, fo ss, mel, al di (?)	24	al di, sp, an, fo ss, mel
28.1	42.9	29	Crystalline Mixtures	di, sp	85	al di, sp, an, fo ss
64.0	21.5	14.5		di, sp, ak	85	al di, mel, sp (tr.), fo ss
82.0	10.7	7.3		di, sp, ak	85	al di, fo ss, mel

TABLE 6 -Continued

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
65	10	25	Mix- Crystalline tures	fo, an, ak	85	al di, fo ss, mel
58.3	35.7	6		geh, di	85	al di, mel, an, sp (tr.)
79.1	17.8	3		geh, ak, di	85	al di, mel, an, sp (?)
86.1	11.9	2		geh, ak, di	85	al di, mel
72.2	23.8	4		geh, ak, di	85	al di, an, mel, sp (tr.)
Temperature: 1230±1.5°C						
38	48	14	Gl. held at 1235.5°C for 7 days	al di, sp, an, mel, fo ss	8	al di, sp, an, mel
Temperature: 1235±1.5°C						
32	43	25	Gl. held at 1100°C for 106 days	al di, sp, an, mel, fo ss	19	al di, sp, fo ss
38	48	14	Gl. held at 1252°C for 3.5 hours	al di, an, fo ss, gl	18	al di, sp, an, mel
Temperature: 1236±1.5°C						
38	35	27	Gl. held at 1236°C for 7 days	al di, an, mel, fo ss, sp (tr.)	7	al di, sp, mel, fo ss
Temperature: 1237±1.5°C						
38	48	14	Gl. held at 1235°C for 14 days	al di, an, mel, sp	8	al di, sp, mel, an

TABLE 6 -Continued

Composition (wt.%)			Starting Material		Time (days)	Final Phase Assemblage
Ak	An	Fo	Initial Treatment	Phase Assemblage		
43	40	17	Gl. held at 1235°C for 18 days	al di, sp, mel, an (tr.)	8	al di, sp, mel, fo ss (?)
42	46	12	Gl. held at 1239.5 °C for 120 hours	al di, an, sp, gl	9	al di, sp, an, mel
Temperature: 1239±1°C						
38	35	27	Gl. held at 1236°C for 14 days	al di, sp, mel, fo ss	7	al di, sp, mel, fo ss
52	35	13	Gl. held at 1241°C for 336 hours	fo ss, mel, al di, gl	14	al di, sp, mel, fo ss
39	39	22	Gl. held at 1241°C for 336 hours	al di, sp, fo ss, gl	14	al di, sp, mel, fo ss

Figure 14. Approximate isothermal section of the join ak-an-fo near 1200°C

More exactly, because of solid solution effect,

Therefore, if the join spinel-aluminous diopside is a tie line, the plane melilite-anorthite-forsterite solid solution can not be a tie plane. Opinions were divided; some believed that spinel is compatible with aluminous diopside while others insisted that the right-hand side of the equation (1) is the stable assemblage.

While studying the phase equilibria of the join grossular-pyrope at atmospheric pressure, Chinner and Schairer (1962) always obtained the assemblage mel+an+fo from the appropriate compositions at subliquidus temperatures, although pyroxenes appeared with other phases in the subliquidus region between 1220°C and 1235°C in some compositions. They regarded those pyroxenes as metastable, and concluded that mel+an+fo ss was the stable assemblage, and presented a "flow sheet", in which reactive invariant points mel+an+fo+py+l and mel+an+fo+sp+l were given (C and D of their Figure 4). From their quenching experiments on di-CaTs compositions between liquidus and solidus temperatures at atmospheric pressure, de Neufville and Schairer (1962) also considered that the assemblage mel+an+fo is stable at atmospheric pressure. Schairer and Kushiro (1965) continued the study of the possibility of spinel coexisting with

aluminous diopside at atmospheric pressure by investigating the join spinel-diopside. They encountered the invariant points, $\text{mel}+\text{an}+\text{fo}+\text{py}+1$ and $\text{mel}+\text{an}+\text{fo}+\text{sp}+1$, as well as the five-phase assemblage $\text{mel}+\text{an}+\text{fo}+\text{sp}+\text{py}$ between 1215°C and 1235°C from the crystalline mixture of the composition $\text{Di}_{70}\text{Sp}_{30}$. Again pyroxene was considered to be metastable and the same conclusion as that of Chinner and Schairer (1962) was arrived at by Schairer and Kushiro, namely, that diopside solid solutions do not coexist with spinel at atmospheric pressure.

Despite evidence for the stability of the assemblage $\text{mel}+\text{an}+\text{fo}$ as at atmospheric pressure by the above authorities, O'Hara and Schairer (1963), assuming the compatibility of spinel with aluminous diopside, proposed three isobaric invariant points, $\text{mel}+\text{an}+\text{sp}+\text{al di}+1$, $\text{mel}+\text{fo}+\text{sp}+\text{al di}+1$, and $\text{an}+\text{fo}+\text{sp}+\text{al di}+1$, to replace Chinner and Schairer's invariant points, $\text{mel}+\text{an}+\text{fo}+\text{py}+1$ and $\text{mel}+\text{an}+\text{fo}+\text{sp}+1$. Using gel as starting material instead of glass, O'Hara and Biggar (1969) presented experimental evidence leading convincingly to the following conclusions: (1) spinel is compatible with aluminous diopside, (2) the isobaric invariant points, $\text{sp}+\text{al di}+\text{an}+\text{fo}+1$, $\text{sp}+\text{al di}+\text{fo}+\text{mel}+1$, and $\text{sp}+\text{al di}+\text{an}+\text{mel}+1$ are distributary reaction, tributary reaction, and eutectic respectively. More recently, Yoder and Schairer (1969) gave additional information in the polyhedron sp-ak-an-fo-di to support

O'Hara and Biggar's scheme of phase equilibria with slight modification.

Result of present study The position of the plane ak-an-fo in the system CMAS is such that the results of subliquidus and subsolidus phase equilibria should clear up the controversy as to whether spinel is compatible with aluminous diopside at atmospheric pressure.

Evidence from liquidus data (figure 4): As mentioned earlier, the primary fields of spinel and aluminous diopside are separated from each other by those of forsterite solid solution and anorthite on the plane ak-an-fo. The liquidus relation does not prove that spinel is compatible with aluminous diopside at temperature immediately below the invariant points, but does not rule out the possibility either, because their primary fields may come together in adjacent regions of the system CMAS, not too far from the plane ak-an-fo.

Evidence from subliquidus data: Important experimental data showing the compatibility of spinel with aluminous diopside are given in Table 7. Although the primary fields of spinel and aluminous diopside do not meet on the liquidus surface, it is possible that both fields may meet on the silica-poor side of the plane ak-an-fo. Glasses in the field of spinel were carried down to the subliquidus temperatures. It was

TABLE 7
EXPERIMENTAL DATA SHOWING THE
COMPATIBILITY OF SPINEL
WITH ALUMINOUS
DIOPSIDE

Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present
Ak	An	Fo			
38	48	14	1247.0	72	fo ss, an, al di, gl
			1244.0	84	fo ss, an, al di, sp, gl
			1240.0	120	an, al di, sp, gl
			1239.0	186	an, al di, sp, gl
			1237.0	192	an, al di, sp, mel
42	46	12	1239.5	120	al di, an, sp, gl
			1237.0	216	al di, an, sp, mel, gl
52	35	13	1241.0	336	fo ss, mel, sp, gl
			1239.0	536	fo ss, mel, al di, sp
39	39	22	1245.0	120	fo ss, al di, gl
			1241.0	336	fo ss, al di, sp, gl
			1239.0	536	fo ss, mel, al di, sp

found that spinel was being dissolved while liquid changed compositions along the univariant line $an+fo\ ss+sp+1$ and disappeared completely when liquid emerged from the silica-rich side of the plane near the point a (figure 4) at about 1267°C. Then the liquid, precipitating forsterite solid solution and anorthite, moves toward the vicinity of point b and aluminous diopside joins the crystallization at about 1255°C. This behavior suggests that, if the primary field of spinel ever meets that of aluminous diopside in the system CMAS, it does not do so on the silica-rich side of the plane $ak-an-fo$, but rather on the silica-poor side and below 1255°C. To confirm this, glass of composition $Ak_{38}An_{48}Fo_{14}$ was

carried down from forsterite solid solution liquidus, across the divariant surface $an+fo\ ss+l$ to the univariant line $an+fo\ ss+al\ di+l$, until those phases were joined by spinel instead of melilite at $1244^{\circ}C$, thus clearly indicating that spinel is compatible with aluminous diopside. At the invariant point, $an+fo\ ss+al\ di+sp+l$, both anorthite and forsterite solid solution were reacting with liquid. After forsterite solid solution was completely resolved, liquid changed composition along the univariant line $an+al\ di+sp+l$ to its pertinent invariant point $an+al\ di+sp+mcl+l$ at $1238^{\circ}C$, where the charge became completely crystallized. The course of crystallization of the composition $Ak_{52}An_{35}Fo_{13}$, likewise in the primary field of forsterite solid solution, was also recorded. It was on the univariant line $fo\ ss+al\ di+mcl+l$ at $1241^{\circ}C$. The crystallization was complete when it was joined by spinel at the invariant point $fo\ ss+al\ di+mcl+sp+l$ at $1240^{\circ}C$, where forsterite solid solution was unstable and partially dissolved. The courses of crystallization of glasses, $Ak_{42}An_{46}Fo_{12}$ and $Ak_{39}An_{39}Fo_{22}$, also encountered the invariant points and univariant line involving spinel and aluminous diopside, as can be seen from Table 7.

To sum up the subliquidus phase equilibria of the polyhedron $sp-ak-an-fo-di$, a "flow sheet" is given

in Figure 15. The nature of the invariant point an+mel+al di+sp+1 was not experimentally determined. Theoretically, whether it is an eutectic or a reaction point depends on its position relative to the plane an-al di-mel. If the extent of solid solution of melilite and aluminous diopside is such that this invariant point falls within subtetrahedron an-mel-al di-wo ss, it is then a reaction point with respect to spinel. If it remains in its pertinent subtetrahedron an-mel-al di-sp, it then becomes a quaternary eutectic point. The temperatures of three invariant points encountered are tabulated in Table 8, along with the data obtained by O'Hara and Biggar (1969) and Yoder and Schairer (1969).

TABLE 8
TEMPERATURES OF QUATERNARY INVARIANT
POINTS OF THE POLYHEDRON
SP-AK-AN-FO-DI

Invariant Points	O'Hara and Biggar (1969)	Yoder and Schairer (1969)	Present Report
an+fo ss+sp+al di+1	1233.5°C	1238+3°C	1244+1°C
fo ss+mel+sp+al di+1	1232°C	1238+3°C	1240+2°C
an+mel+sp+al di+1	1230°C	1238+3°C	1238+2°C

Evidence from subsolidus data: Chinner and Schairer (1962), de Neufville and Schairer (1962), and Schairer and Kushiro (1965) considered that the assem-

Figure 15. The "flow sheet" of the polyhedron Sp-Mel-An-Fo ss-AlDi

blage an+mel+fo ss was more stable than the assemblage sp+al di, without demonstrating the reaction of equation (1) from left to right. What they established was that the assemblage an+mel+fo ss was more stable than glasses, but not necessarily more stable than the assemblage sp+al di.

Effort has been made by the writer to show that the assemblage sp+al di is more stable than the assemblage an+mel+fo ss by demonstrating the reaction of equation (1) from right to left. The starting material consisted of various combinations of aluminous diopside, anorthite, forsterite solid solution, forsterite, diopside, akermanite, melilite, and spinel. After long period of firing at subsolidus temperatures, the end products were always sp+al di+fo ss+an, sp+al di+fo ss+mel, or sp+al di+an+mel, as can be seen in Table 6 in previous section. Thus, the fact that the assemblage sp+al di is more stable than the assemblage an+mel+fo ss is demonstrated. Consequently, the planes sp-al di-mel, sp-al di-an, and sp-al di-fo ss are tie planes and the polyhedron sp-ak-an-fo-di is primarily subdivided into three subtetrahedra sp-al di-an-mel, sp-al di-an-fo ss, and sp-al di-mel-fo ss. The plane ak-an-fo intersects these subtetrahedra and three triangular four-phase regions are formed. In addition, there are several

other regions, as explained in the next three sections.

The three-phase region

Due to the continuous solid solution from akermanite toward gehlenite, limited solid solution from diopside toward Calcium Tschermak's molecule, and limited solid solution of monticellite in forsterite, a three-phase volume which is a prism bounded by melilite, forsterite solid solution, and aluminous diopside, is generated. It cuts the plane ak-an-fo in a triangle Fo-Ak-c (figure 13 and 14) in which melilite, forsterite solid solution, and aluminous diopside are the stable phases. Pertinent experimental data can be found in Table 6. Devitrification of glasses of this region always gives these three phases. A mixture of crystalline forsterite, akermanite, and anorthite, $\text{Ak}_{65}\text{An}_{10}\text{Fo}_{25}$, lying in this region, was held at 1200°C for eighty five days. Anorthite was eliminated, aluminous diopside developed, and akermanite became aluminous. Two mixtures of crystalline spinel, diopside, and akermanite, corresponding to $\text{Ak}_{64}\text{An}_{21.5}\text{Fo}_{14.5}$ and $\text{Ak}_{82}\text{An}_{10.7}\text{Fo}_{7.3}$, were also held at 1200°C for eighty five days. Spinel was eliminated in the second composition, forsterite solid solution developed, and diopside and akermanite became aluminous. The extent of this region depends on the extent of solid solution of melilite, aluminous diopside,

and forsterite solid solution, which, in turn, are functions of temperature. The position of the line Fo-c was determined experimentally. It moves closer to the Fo-Ak sideline as the temperature decreases.

Four-phase assemblage melilite-anorthite-wollastonite solid solution-aluminous diopside

Part of the plane Ak-An-Fo, Ak-An-d (figure 13 and figure 14), falls within the subtetrahedron an-mel-wo ss-al di, as affected by the solid solution of melilite and aluminous diopside. The join an-ak was investigated by de Wys and Foster (1957) and was reported to be a true binary system with akermanite and anorthite coexisting below the binary eutectic point, 1234°C. Yoder re-studied this join in 1968 and found that it showed quaternary behavior with the appearance of pyroxene and wollastonite solid solution in addition to melilite and anorthite.

Subliquidus and subsolidus phase equilibria of two glasses and two crystalline mixtures, belonging to this region, have been investigated in this study. The experimental data can be found in Tables 5 and 6, and, for convenience, are regrouped in Table 9.

With the decreasing temperature, glass of the composition $Ak_{54}An_{46}$ and crystalline mixture of the composition $Ak_{50}An_{50}$ pass through the divariant surface

TABLE 9

EXPERIMENTAL DATA PERTINENT TO THE
SUBTETRAHEDRON ANORTHITE-MELILITE-
WOLLASTONITE SOLID SOLUTION-
ALUMINOUS DIOPSIDE

Composition (wt.%)			Temp. (°C)	Time (days)	Starting Material	Final Phase Assemblage
Ak	An	Fo				
50	46	0	1244.0	1	Devitrified Glasses	mel, an, gl
			1239.0	6		mel, an, al di, gl
			1225.0	30		mel, an, pwo ss, gl
			1180.0	30		mel, an, wo ss, al di
70	29	1	1245.0	1	Devitrified Glasses	mel, gl
			1225.0	30		mel, an, gl
50	50	0	1215.0	39	an, ak	mel, an, pwo ss, gl
			1200.0	46	mel, an, pwo ss, gl	mel, an, al di, wo ss
58.5	40.1	1.4	1240.0	8	an, ak, sp, di	mel, an, al di, gl
			1215.0	39	an, ak, sp, di	mel, an, pwo ss, gl
			1200.0	46	mel, an, pwo ss, gl	mel, an, wo ss, al di

mel+an+1 and the univariant line mel+an+pwo ss+1 to the invariant point an+mel+pwo ss+wo ss+1 where pwo ss inverts to wo ss, and then they become completely crystalline at the invariant point an+mel+wo ss+al di+1, when aluminous diopside joins the crystallization. A crystalline mixture of the bulk composition $Ak_{58.5}An_{40.1}Fo_{1.4}$ encounters, on the decreasing temperature, the univariant line an+mel+al di+1, which is in a reaction relation with respect to aluminous diopside. After aluminous diopside is entirely resolved, liquid changes its composition across the divariant surface an+mel+1 and meets the univariant line an+mel+pwo ss+1. Pseudowollastonite solid solution inverts to wollastonite solid solution at the invariant point an+mel+wo ss+pwo ss+1. Liquid then changes its composition along the univariant line an+mel+wo ss+1 and reaches the invariant point an+mel+wo ss+al di+1, where aluminous diopside reappears, and is exhausted at this point.

Three-phase assemblage melilite-aluminous diopside-wollastonite solid solution

The assemblage melilite-aluminous diopside-wollastonite solid solution is stable in the area Ak-c-d (figures 13 and 14).

THE COMPOSITION OF ALUMINOUS DIOPSIDE

General Statement

The experimental study of the aluminous diopside has been inspired by the fact that the natural diopsides have been found to contain considerable amount of alumina, the maximum being 15.75 wt% Al_2O_3 or 42.7 mol% CaTs as recorded by Knopf and Lee (1957). It was Osborn who first pointed out in 1942 that the synthetic diopside on the join anorthite-diopside was aluminous. Zvetkov (1945) obtained from melts of mixed oxides, aluminous diopside containing as much as eighteen to nineteen weight percent Al_2O_3 or forty mole percent CaTs. According to Chang (1952), diopside appeared with liquid on the join anorthite-monticellite. Its composition was estimated by the present writer, based on Sakata's determinative curve, to be about $\text{Di}_{65}\text{CaTs}_{35}$. Segnit (1953) carried out a study on the limit of solid solution of aluminous diopsides in the plane $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ by crystallizing homogeneous glasses below their solidus temperatures for periods varying from two hours to several days and placed the limit of solid solution at 13 wt% Al_2O_3 , 25 mol% CAS, and 20 mol% MAS respectively. Also devitrifying glasses

on the join diopside-CaTs at 1200°C for several hours, Sakata was able to synthesize aluminous diopside of the composition $\text{Di}_{60}\text{CaTs}_{40}$ and provided the determinative curves (1957). Similar synthetic studies were made by investigators at the Geophysical Laboratory and was extended into the subliquidus region; however, the same technique--the devitrification of glasses at subsolidus temperatures--was still employed. Hytonen and Schairer (1960) concluded that with decreasing temperature the amount of CAS in diopside increases at least to the solidus, and that at higher temperatures the diopsides are richer in MgSiO_3 than at lower temperatures. They further considered that the aluminous diopside, obtained by crystallizing homogeneous glasses for seven to fifty days at various temperatures between 1050°C and 1150°C, are metastable. From the data presented by O'Hara and Schairer (1962), the maximum solid solution of CAS, Al_2O_3 , and MAS in diopside was estimated to be 17.2 mol%, 5 mol%, and 7.8 mol% respectively. They also noted the ease of formation and subsequent persistence of metastable aluminous pyroxenes below 1200°C.

The problem of the attainment of equilibrium is perhaps responsible for the great diversity of opinion on the limit of solid solution of aluminous diopside. As a matter of fact, none of the mentioned investigators has demonstrated the attainment of equilibrium. Conse-

quently, only those reported compositions of aluminous diopside coexisting with fairly large amount of liquid are acceptable, while those, either coexisting with a small amount of liquid or existing in a complete crystalline assemblage, are subject to question.

Experimental Methods

To demonstrate the attainment of equilibrium, the following technique was used in the present study. Two batches of powdered, devitrified glasses of the same bulk composition or of the same subtetrahedron were selected. One of these, in addition to other crystalline phases, contained an aluminous diopside richer in the CAS component than the expected equilibrium composition. The other was poorer in the CAS component than the expected equilibrium composition. Both were held at the same temperature for an appropriate length of time. Equilibrium is demonstrated when the compositions of these two initially different metastable aluminous diopsides become the same. This technique is adopted when less than one third of the charge is liquid and the reaction is found to be very sluggish. When more than one third of the charge is liquid, it is believed that the equilibrium can be readily attained, so the ordinary quenching method was used.

Determination of The Composition of Aluminous Diopside

Optical Examination

When aluminous diopsides are coarse enough to be identified under the petrographic microscope, the alpha indices can be measured, and compositions are obtained on the basis of Hay's optical data (1966). The results are tabulated in Table 10. The accuracy is estimated to be ± 2 mol% CAS. These results, as well as those from x-ray diffraction and microprobe analyses, are discussed in a later section.

X-ray Diffraction

The lattice constants have been correlated with the compositions for aluminous diopside from diopside toward CaTs by Sakata (1957) and by Clark, Schairer, and de Neufville (1960). The results of these two previous studies are in good agreement with each other, and Sakata's data were used for the present study. Powder mounts of the experimental charges were x-rayed by Cu K α radiation, scanning at a speed of one half degree 2θ per minute. Using the 200 and 220 reflections ($31.72^\circ 2\theta$ and $45.48^\circ 2\theta$ respectively) of NaCl as internal standard, the 2θ positions of the $22\bar{1}$, 002, and 131 reflections of aluminous diopside were measured, which, in turn, gave the mole percent CAS in solid solution with diopside. The results are presented in Table 11. The error arising

TABLE 10
COMPOSITION OF ALUMINOUS DIOPSIDE
FROM OPTICAL DATA

Composition (wt.%)			Temp. (°C)	Time (hrs.)	Phases Present	alpha	Aluminous Diopside	
Ak	An	Fo					Di	CaTs
47	44	9	1253.0	2.0	al di, gl	1.670	86.7	13.3
			1249.0	2.0	al di, gl	1.670	86.7	13.3
			1242.0	21.0	al di, mel, an, gl	1.674	77.8	22.2
			1240.0	161.0	al di, mel, an, gl	1.674	77.8	22.2
45	45	10	1244.5	17.5	al di, gl	1.672	82.2	17.8
			1250.0	2.0	al di, gl	1.670	86.7	13.3
47	46	7	1243.0	17.0	al di, an, gl	1.672	82.2	17.8
			1240.0	161.0	al di, mel, an, gl	1.674	77.8	22.2
45	47	8	1246.0	5.0	al di, an, gl	1.672	82.2	17.8

TABLE 11

COMPOSITIONS OF ALUMINOUS DIOPSIDE FROM X-RAY DATA
 Temperature: 1200.0°C Duration: 85 days

Composition (wt.%)			Starting Material						Final Product					
			Phase	Aluminous Diopside					Phase	Aluminous Diopside				
				2θ (degree)		Comp.mol%				2θ (degree)		Comp.mol%		
Ak	An	Fo	Assem.	221	002	131	Di	CaTs	Assem.	221	002	131	Di	CaTs
28.1	42.9	29	sp, di	35.6	34.8	100	0		sp, al di an, fo ss	35.85	35.44	35.16	77	23
64.0	21.5	14.5	sp, di, ak	35.6	34.8	100	0		sp, mel, fo ss, al di	35.85	35.45	35.17	75	25
82	10.7	7.3	sp, di, ak	35.6	34.8	100	0		mel, al di	35.79	35.48	35.09	83	17
65	10	25	fo, ak, an	-	-	-	-	-	mel, al di fo ss	-	-	35.08	84	16
40	47.5	12.5	mel, al di	35.95	35.36		58	42	sp, al di mel, an	35.87	35.45	35.20	72	28
44	44	12	mel, al di	35.95	35.36		58	42	sp, al di mel, an	35.90	35.48	35.21	70	30
56	31	13	mel, al di, fo ss	35.95	35.36		58	42	sp, mel, al di, fo ss	35.86	35.45	35.19	74	26

from the measurement of the positions of the reflections is $\pm 0.01^\circ 2\theta$ which correspond to ± 1.2 mol% CAS.

Electronprobe Microanalysis

Direct access to the composition of aluminous diopside in equilibrium with the liquid is provided by the use of the electron microprobe technique. The size of the crystals of aluminous diopside crystallizing from melts near the liquidus temperatures is generally less than fifteen microns, but occasionally crystals larger than thirty microns can be found. Uncrushed quenching charges were mounted in bakelite and polished, so that the crystals of aluminous diopside can be seen under reflected light. Homogeneous glasses of the compositions 43.81% SiO_2 , 14.80% MgO , 7.33% Al_2O_3 , 34.06% CaO and 43.33% SiO_2 , 17.89% MgO , 17.59% Al_2O_3 , 21.19% CaO were used as external standards and were also mounted in bakelite and polished. The polished surfaces were coated with a thin film of carbon to conduct the current. An ARL electron microprobe was used in the experiment. Operating the probe at 25 KV and using a KAP analyzing crystal and a proportional counter, the peak intensities of Al and Mg $K\alpha$ radiations from two external standards were measured and plotted against the weight percentages of their oxides to form the calibration lines (figure 16). The peak intensities of Al and Mg $K\alpha$ radiations from aluminous diopside were also recorded under the same

TABLE 12

COMPOSITION OF ALUMINOUS DIOPSIDE
FROM MICROPROBE DATA

No.	Standards					
	Composition (wt.%)				Intensities (cts/10sec)	
	SiO ₂	MgO	Al ₂ O ₃	CaO	Mg K α	Al K α
1	43.81	14.80	7.33	34.06	1360	190
2	43.33	17.89	17.59	21.19	1750	850

Specimens										
	Composition (wt.%)			Temp. (°C)	Time (hrs)	Phases Present	Aluminous Diopside			
	Ak	An	Fo				Inten. cts/10sec Comp.(wt.%)			
							Mg K α	Al K α	MgO	Al ₂ O ₃
1	47	44	7	1247	24	al di, gl	1600	380	16.0	10.0
2	45	45	10	1246	24	al di, gi	1550	390	15.5	10.5

Figure 16. Determination of the weight percentages of MgO and Al_2O_3 in aluminous diopside from electron microprobe

▲ Standards

• Specimens

operating conditions and the weight percentages of Al_2O_3 and MgO in aluminous diopside were read directly from the calibration lines. The experimental data are given in Table 12 and Figure 15. Assuming that the errors inherent from the generation of x-ray from the specimens and from the experimental arrangement in the instrument are minimized by the use of external standards, the accuracy of the present experiment is believed to be within ± 0.5 wt.% oxides.

Discussion

The optical, x-ray diffraction, and microprobe data are incorporated in Figure 17, which shows the variation of the composition of aluminous diopside along the join diopside-CaTs with the temperature. The amount of CAS in diopside increases as the temperature decreases from the liquidus temperature to the temperature of the invariant point. This is in agreement with Hytonen and Schairer's observation (1960). With deficiency of data between 1230°C and 1240°C , it is inferred that the limit of solid solution of aluminous diopside extends toward CAS to a maximum of about 32 mol% CAS at the temperature of the invariant point, 1238°C , and then decreases with decreasing temperature to 25.5 mol% CAS at 1200°C .

It must be born in mind that the foregoing discussion is based on the assumption that the composi-

Figure 17. Variation of composition of aluminous diopside with the temperature

- Optical data; length indicates the range of experimental uncertainty.
- Microprobe data; length indicates the range of experimental uncertainty.
- X-ray diffraction data; the initial composition was diopside. The point of arrow indicates its composition at the end of experiment.
- ← X-ray diffraction data; the initial composition was $\text{Di}_{58}\text{CaTs}_{42}$. The point of arrow indicates its composition at the end of experiment.

tion of aluminous diopside varies along the join diopside-CaTs only. This is by no means without question. The departure of the composition of aluminous diopside from this join has already been noted (O'Hara and Schairer, 1962; Schairer and Kushiro, 1965). The present data also suggest such a further complication of the composition of aluminous diopside, due to the considerable variability of MgO content in aluminous diopside. The microprobe data (figure 18 and table 12) indicate that aluminous diopside crystallizing from melt at 1246°C and 1247°C is richer in MgO than it would be if it is assumed to lie on the join diopside-CaTs. On the contrary, location of aluminous diopside on the CaO-rich side of the join diopside-CaTs is suggested by the fact that an initial assemblage of spinel and diopside of the bulk composition of $\text{Ak}_{28.1}\text{An}_{42.9}\text{Fo}_{29}$ gives a final assemblage of spinel+aluminous diopside+anorthite+forsterite solid solution at 1200°C. This is supported by a run in which a glass of the composition $\text{Ak}_{32}\text{An}_{43}\text{Fo}_{25}$ devitrified to an assemblage of spinel+aluminous diopside+forsterite solid solution at 1235°C.

Although the present data are not enough to draw any clear-cut conclusions, they do cast some light on the composition of aluminous diopside. While the maximum amount of CAS in aluminous diopside remains unsolved,

Figure 18 Limit of solid solution of aluminous diopside in the plane CS-MS-A. Solid curves: O'Hara and Schairer (1962). Broken and dotted curve: Segnit (1953) ○ Present data from electron microprobe.

a planar variation of the composition of aluminous diopside seems clear. Further progress must await the reliable two-dimensional analytical methods for the determination of the composition of aluminous diopside.

THE COMPOSITION OF MELILITE

General Statement

Ferguson and Buddington (1920) reported that the binary solid solution between akermanite and gehlenite is complete with a minimum at $Ak_{74}Geh_{26}$ and at $1388^{\circ}C$ on the liquidus surface. They have also correlated indices of refraction with the composition for melilite.

De Neufville and Schairer (1962) have found that the composition of melilite in equilibrium with aluminous diopside+anorthite+forsterite solid solution was $Ak_{89}Geh_{11}$, and it ranged from $Ak_{89}Geh_{11}$ to $Ak_{69}Geh_{31}$ in the assemblage melilite+anorthite+forsterite solid solution. Chinner and Schairer reported in 1962 that the composition of melilite changed from Ak_0Geh_{100} to $Ak_{75}Geh_{25}$ in the crystalline assemblage melilite+anorthite-wollastonite solid solution and was $Ak_{75}Geh_{25}$ in the assemblage melilite+anorthite+forsterite solid solution. Yoder and Schairer (1969) have also presented the change of composition of melilite in the bulk compositions ranging from $Ak_{100}Sp_0$ to $Ak_{80}Sp_{20}$.

Since evidence has been presented to show that mel+an+al di+sp, mel+fo ss+al di+sp, and an+fo ss+al di

+sp are the stable assemblages in the polyhedron sp-ak-an-fo-di at atmospheric pressure, it is desired to know the equilibrium composition of melilite in the first two assemblages.

Experimental Methods

The same techniques described and used in the previous chapter to demonstrate the equilibrium for the composition of aluminous diopside were also used in the present chapter to demonstrate the equilibrium for the composition of melilite. Three additional crystalline mixtures whose compositions lie on the plane ak-an-fo were prepared by mixing crystalline akermanite, diopside, and gehlenite in appropriate proportions (8, 9, and 10 of Table 1). Equilibrium is demonstrated when an intermediate melilite is formed to replace akermanite and gehlenite.

Determination of Composition of Melilite

Measurement of index of refraction, ω , of melilite is satisfactory, although difficulty arises when melilite approaches isotropy optically near the temperature of the invariant point. The compositions of melilites are obtained from their ω 's, based on the determinative curve provided by Ferguson and Buddington (1920). The results are given in Table 13. The accuracy is ± 2.0 wt.% C_2AS .

TABLE 13

COMPOSITIONS OF MELILITE FROM OPTICAL DATA

Composition (wt.%)			Temp. (°C)	Time (hours)	Starting Material			Final Product				
Ak	An	Fo			Phase Assemb.	Melilite		Phase Assemb.	Melilite			
						W	Ak		Geh	W	Ak	Geh
55	40	5	1243.5	18.0	Devitrified Glasses Fo ss+an+mel+glass	W's can not be measured with sufficient accuracy		mel+glass	1.636	92	8	
70	29	1	1245.0	25.0					1.635	94	6	
			1252.0	24.0					1.635	94	6	
55	40	5	1270.5	2.0					1.634	96	4	
81	14	5	1395.0	1.8					1.632	100	0	
73	20	7	1366.0	1.7					1.632	100	0	
62	33	5	1312.0	2.0					1.633	98	2	
			1245.0	24.0					1.635	94	6	
56	31	13	1302.5	1.5					1.633	98	2	
60	25	15	1327.0	1.8					fo ss, mel, gl	1.633	98	2
50	38	12	1255.0	18.0					1.635	94	6	
			1245.0	20.0					1.635	94	6	
			1242.0	19.0					mel, gl	1.637	90	10
52	35	13	1241.0	240.0					al di, fo ss	1.637	90	10
38	48	14	1237.5	192.0					mel, sp al di, an	1.638	88	12
56	31	13	1215.0	360.0	mel, fo ss, al di	1.638	88	12	mel, sp, al di, fo ss	1.637	90	10
64.0	21.5	14.5	1215.0	600.0	sp, di, ak	1.632	100	0	mel, sp, al di fo ss	1.636	92	8

TABLE 13 -Continued

Composition (wt.%)			Temp. (°C)	Time (days)	Starting Material				Final Product			
Ak	An	Fo			Phase Assemb.	Melilite			Phase Assemb.	Melilite		
						W	Ak	Geh		W	Ak	Geh
44	44	12	1215.0	15	mel, an, al di	1.638	88	12	mel, an, sp, al di	1.637	90	10
40	47.5	12.5	1215.0	15	mel, al di	1.638	88	12		1.637	90	10
58.5	40.1	1.4	1215.0	25	sp, di, an, ak	1.632	100	0	mel, an, pwo ss, gl	1.635	94	6
50	50	0	1215.0	25	an, ak	1.632	100	0		1.635	94	6
55	40	5	1200.0	85	mel, gl	1.638	88	12	mel, al di,	1.636	92	8
70	29	1	1200.0	85	mel, gl	1.637	90	10		1.636	92	8
62	33	5	1200.0	85	mel, an, al di	1.638	88	12		1.636	92	8
40	47.5	12.5	1200.0	85	mel, al di	1.638	88	12	an, mel, al di,	1.636	92	8
44	44	12	1200.0	85	mel, al di	1.638	88	12	an, sp	1.636	92	8
56	31	13	1200.0	85	mel, fo ss, al di	1.638	88	12	mel, sp, al di, fo ss	1.636	92	8
64.0	21.5	14.5	1200.0	85	ak, di, sp	1.632	100	0		1.636	92	8
81	14	5	1200.0	85	mel al di	1.636	92	8	mel, al di	1.635	94	6

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TABLE 13 -Continued

Composition (wt.%)			Temp. (°C)	Time (days)	Starting Material			Final Product				
Ak	An	Fo			Phase Assemb.	Melilite		Phase Assemb.	Melilite			
						W	Ak		Geh	W	Ak	Geh
73	20	7	1200.0	85	mel, al di	1.636	92	8	mel, al di	1.635	94	6
82	10.7	7.3	1200.0	85	ak, di, sp	1.632	100	0	<hr/> mel, al di, fo ss	1.634	96	4
65	10	25	1200.0	85	fo, an, ak	1.632	100	0	<hr/> fo ss	1.634	96	4
58.5	40.1	1.4	1200.0	85	ak, di, an, sp	1.632	100	0	<hr/> mel, al di, wo ss, an	1.636	92	8
50	50	0	1200.0	85	an, ak	1.632	100	0	<hr/> an	1.636	92	8
58.3	35.7	6	1200.0	54	di, geh	1.669	0	100	<hr/> mel, al di, sp, an	1.636	92	8
72.2	23.8	4	1200.0	54	ak, di, geh	1.632 1.669	100 0	0 100	<hr/> an	1.636	92	9
79.1	17.9	3	1200.0	54	ak, di, geh	1.632 1.669	100 0	0 100	<hr/> mel, al di	1.635	94	6
86.1	11.9	2	1200.0	54	ak, di, geh	1.632 1.669	100 0	0 100	<hr/>	1.634	96	4
39	39	22	1100.0	106	mel, sp, fo ss, an al di	1.638	88	12	mel, sp, fo ss, al di	1.636	92	8

TABLE 13 -Continued

Composition (wt.%)			Temp. (°C)	Time (days)	Starting Material				Final Product			
Ak	An	Fo			Phase Assemb.	Melilite			Phase Assemb.	Melilite		
						ω	Ak	Geh		ω	Ak	Geh
64	21.5	14.5	1100.0	58	ak, di, sp	1.632	100	0	mel, sp, an, al di	1.634	96	4
58.5	40.1	1.4	1100.0	58	ak, di, sp, an	1.632	100	0	mel, an wo ss, al di	1.634	96	4
50	50	0	1100.0	58	ak, an	1.632	100	0	mel, an wo ss(?) al di	1.634	96	4

Discussion

Equilibrium was demonstrated for the composition of melilite coexisting with $sp+al$ $di+fo$ ss and with $sp+al$ $di+an$ at $1200^{\circ}C$. It is found that the equilibrium compositions of melilites in these two crystalline assemblages are the same, namely, $Ak_{92}Geh_8$ at $1200^{\circ}C$.

The variation of the composition of melilite with temperature is shown in Figure 19. The composition of melilite changes gradually from Ak_{100} above $1350^{\circ}C$ to $Ak_{88}Geh_{12}$ near the temperature of the invariant point, $1238^{\circ}C$. Then the amount of the gehlenite component in melilite decreases with decreasing temperature to about 4 wt% C_2AS near $1100^{\circ}C$. The composition of melilite that can coexist with forsterite solid solution ranges, therefore, from pure akermanite to $Ak_{88}Geh_{12}$.

It is also found that the gehlenite component in melilite increases continuously in the three-phase region as the Al_2O_3 content of the bulk composition increases.

Figure 19. Variation of the composition of melilite with temperature. The arrows indicate the direction of change of the composition of melilite, and the points indicate the final compositions. —●— Optical data

CONCLUSIONS

1. Primary fields of anorthite, aluminous diopside, spinel, melilite, forsterite solid solution, and monticellite solid solution are found on the liquidus surface of the join akermanite-anorthite-forsterite.

2. The quaternary univariant lines spinel+anorthite+forsterite solid solution+liquid, anorthite+forsterite solid solution+aluminous diopside+liquid, melilite+aluminous diopside+forsterite solid solution+liquid, melilite+anorthite+aluminous diopside+liquid, and melilite+monticellite solid solution+forsterite solid solution+liquid pierce the join akermanite-anorthite-forsterite.

3. Spinel is compatible with aluminous diopside at atmospheric pressure, and there exist the subtetrahedra Spinel- $\text{Di}_{68}\text{CaTs}_{32}$ -Fo ss-Anorthite, Spinel- $\text{Di}_{68}\text{CaTs}_{32}$ -Fo ss-Ak₈₈Geh₁₂, and Spinel- $\text{Di}_{68}\text{CaTs}_{32}$ -Ak₈₈Geh₁₂-Anorthite.

4. A "flow sheet", showing the quaternary invariant and univariant phase equilibria of the polyhedron Spinel-Ak₈₈Geh₁₂-Anorthite-Fo ss- $\text{Di}_{68}\text{CaTs}_{32}$, is given in Figure 14.

5. Limit of solid solution of diopside toward

Calcium Tschermak's molecule is predicted to be 32 mol% CAS at atmospheric pressure.

6. The composition of melilite that can coexist with forsterite solid solution ranges from pure akermanite to $\text{Ak}_{88}\text{Geh}_{12}$.

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